

## Part 11 Iodimetric Analysis of Dialkyl and Dicumenyl Peroxides†

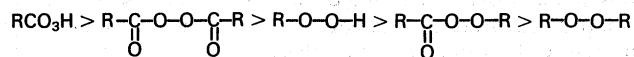
Leonard S. Silbert‡

US Department of Agriculture, ARS, Eastern Regional Research Center, 600 East Mermaid Lane, Philadelphia, PA 19118, USA

Dialkyl peroxides, the most stable and least reactive of the peroxides, slowly react iodimetrically at elevated temperatures. A simple rapid thermal reaction of dialkyl peroxide with iodide ion was developed with either  $\text{HClO}_4$  or  $\text{Fe}^{3+}$  as catalyst. The iodimetric titrations gave quantitative results in 2–20 min, depending on the catalyst concentration, temperature and peroxide structure. The order of decreasing peroxide reactivity and increasing stability based on structure was dialkyl, *tert*-butyl alkyl, diaralkyl, di-*tert*-butyl. The dialkyl peroxides, the most reactive in this analytical procedure, did not require catalysis, but quantification of this class of peroxides was limited to those soluble in the acetic acid solvent. The method is not applicable to insoluble peroxides, which exceed 20 carbon atoms.

**Keywords:** Dialkyl peroxides; iodimetry; catalysis; gas-liquid chromatography

Iodimetry, the iodide reduction of the peroxide bond with associated liberation of iodine, has been widely used for the convenient and accurate determination of peroxides.<sup>1</sup> Because of bond energy differences in peroxide bond strength, peroxides react with iodide ion at different rates. For an aliphatic series of derivatives, the order of increasing O–O bond strength parallels the following decreasing order of reactivity.<sup>2,3</sup>



The first three species rapidly react with iodide ion at room temperature but peroxyesters require  $\text{Fe}^{3+}$  catalysis<sup>4</sup> or elevated temperature<sup>5</sup> for rate acceleration whereas dialkyl peroxides are unreactive.

The first successful quantitative iodimetric determination of a dialkyl peroxide was reported for di-*tert*-butyl peroxide in HI solution.<sup>6</sup> Subsequently, Mair and Graupner<sup>5</sup> in a detailed study of several peroxides that included three aralkyl members [dicumenyl, dicumenyl and bis(diisopropylphenyl) peroxides] and two aliphatics (the transannular peroxide, ascaridole, and di-*tert*-butyl peroxide) developed three methods to cover the range of peroxide reactivities: a modification of the propan-2-ol-acetic acid- $\text{I}^-$  method of Wagner *et al.*<sup>7</sup> (Method 1) for those easily reduced;  $\text{HCl}$ -acetic acid- $\text{I}^-$  at room temperature (Method 2) for those moderately easily reduced; and the latter at 120 °C (Method 3) for difficult to reduce peroxides. These methods in execution are comparatively more complicated than simple iodine liberation methods, namely their requirement of a specially designed vessel equipped with a cool-joint Liebig condenser for refluxing at 120 °C on a hot-plate, an inlet on the vessel for maintaining an inert atmosphere under constant gas flow, use of solid sodium iodide (instead of aqueous solution) and 37%  $\text{HCl}$  for liberating HI, inclusion of added water to control iodine-liberating side reactions from aralkyl and terpene related alcohols (the product of iodide reduction of aralkyl peroxides) and in Method 3 long reaction times (50 min).

Hiatt *et al.*<sup>8</sup> later described the iodimetric determination of di-*sec*-butyl peroxide catalysed by a metal ion ( $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  or  $\text{Cu}^{2+}$ ) in 90 + 10 propan-2-ol-acetic acid- $\text{I}^-$  solution but they included no experimental data in support of the stated quantification ( $100 \pm 2\%$  of theoretical iodine). The additional extension of the method to the more hindered di-*tert*-butyl peroxide and *tert*-butyl cyclohexyl peroxide gave, 60 and 43%, respectively, of the theoretical amount of iodine.

In prior years, a disadvantage in the application of iodimetric titration to the determination of dialkyl peroxides has been the absence of a confirming alternative quantitative method capable of determining the accuracy. The unreliability of the above iodimetric methods became apparent in a programme on the synthesis and analysis of dialkyl peroxides, which necessitated the development of methods for independent purity determinations<sup>9</sup> using gas-liquid chromatography (GLC) and high-performance liquid chromatography (HPLC). A simplification of the procedures of Mair and Graupner<sup>5</sup> had been attempted using standard iodine flasks in place of the specially designed vessel used previously but the results obtained were not reliable when judged in comparison with chromatographic methods. As the latter values could serve as accurate standards for confirmation of dialkyl peroxide contents, a study was initiated to modify the classical method of Wheeler<sup>10</sup> for simplification and acceleration of the reaction. The present study improved the iodimetry by substitution of perchloric acid for 37%  $\text{HCl}$  and of  $\text{Fe}^{3+}$  as catalyst combined with time and temperature parameters for developing optimum conditions. One aim was directed to developing iodimetric methods that would differentiate specific dialkyl peroxide structures.

### Experimental

#### Reagents

Analytical-reagent grade chemicals were used. Saturated solutions of sodium iodide, US Pharmacopeia or analytically pure grade, were prepared. High purity acetic acid was obtained from Mallinckrodt ( $5 \times 10^{-6}\%$  Fe). Acetic acid solutions of  $\text{Fe}^{3+}$  were % m/v  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , which were used at appropriate concentrations (listed in Tables 1, 4, 5 and 6). Fresh solutions were prepared every 2–4 d for the 0.05–0.2% solutions owing to chemical instability resulting in iron(III) oxide precipitation that altered the  $\text{Fe}^{3+}$  concentrations.

	Amount of 70% HClO <sub>4</sub> added/ml	Amount of FeCl <sub>3</sub> ·6H <sub>2</sub> O in acetic acid (% m/v)	Time/ min	Peroxide reacted in solvent (%)	
				Distilled acetic acid	Undistilled acetic acid
<i>A†. Effect of HClO<sub>4</sub></i>					
	—	—	10	—	48
	0.1-0.2	—	5-15	—	90, 93, 95, 97
	0.5	—	5	96.5, 97.3, 97.8, 98.3 99.7, 99.7, 100.5, 100.5, 101.0, 103.1 $\bar{x} = 99.4 (s = 1.98)$	95.8, 98.3, 99.0, 99.6 100.1, 102.8, 105.1, 106.0 $\bar{x} = 100.8 (s = 3.50)$
	0.5	—	10	—	106
	0.5 (H <sub>2</sub> O)‡	—	15	—	73
	0.8-1.0	—	1-5	—	94, 95, 102, 114
<i>B†. Effect of HClO<sub>4</sub> and Fe<sup>3+</sup></i>					
	0.5	2 × 10 <sup>-3</sup>	5	91.7, 95.0, 95.2 97.4, 99.7, 103.7 $\bar{x} = 97.0 (s = 4.99)$	—
	0.2	0.1	5	96.2, 97.5, 106.5	—
	0.2	0.1	15, 20	100, 108	—
	0.5	0.2	5	96.2, 98.7, 101.5	—

\* 99.6% by HPLC.

† Blanks were 5% correction to titre.

‡ Total water content, 28%, by dilution with water (7 ml).

**Table 2** Effect of perchloric acid on iodine liberation by di-*tert*-butyl peroxide\*† at 100 °C

Amount of 70% HClO <sub>4</sub> added/ml	Time/ min	Amount of peroxide reacted (%)
0.5	15	90.3, 95.5
	30	89.3, 91.0, 95.9, 96.7
1.0	15, 20	95.3, 94.6
2.0	10, 15	96.2, 98.7
	20	97.3, 96.0, 98.3 $\bar{x} = 97.2 (s = 1.15)$
3.0	30	91.5

\* 99.9% minimum *via* GLC.

† B.p. 109 °C (atm); see ref. 11, p. 42.

### Equipment

Iodine flasks (200–250 ml) equipped with ST 24/40 joints and ST 24/40 barrel-shaped flat-topped stoppers with side grooves for gripping were obtained from Scientific Glass and Instruments. The flasks weighed under 95 g for direct weighing of samples. To prevent stopper ejection during heating, each flask with an inserted stopper was placed onto the steam-bath (or into a temperature-controlled water-bath for lower temperatures), the well was wetted with acetic acid and the flask and stopper were held in place by downward pressure of a clamp jaw swivelled on top of the stopper head. After reaction, the flask and stopper were hand-held tightly as the clamp was swivelled off.

Chromatographic methods such as GLC and HPLC have been studied for several peroxide series, details of which will be published elsewhere.<sup>9</sup> The small chain peroxides, *viz.*, dihexyl, dioctyl and *tert*-butyl octyl peroxides were determined by GLC at a column temperature of 50 °C [quartz capillary column: 12 m × 0.2 mm i.d. with a 0.33 µm coating of methyl silicone fluid OV 101 (HP Part No. 1901-60010) in a Hewlett-Packard 5830 A instrument equipped with a capillary inlet system, Part No. 18835B, a flame-ionization detector (200 °C) and an injector port (150 °C)]. The peroxides indicated were thermally stable under these conditions. The GLC and HPLC values obtained were reproducible on duplicate determinations to within ±0.3%.

### Procedure

#### General method

In the general non-catalytic method, a sample (1.2–1.6 mequiv) was weighed; this was followed by addition of acetic

acid (15 ml) and concentrated aqueous sodium iodide solution (2 ml); the sample was then sparged with N<sub>2</sub> (15 s). For heated samples, the flask was immersed in the water-bath, the stopper was properly secured as described above and the well was partially filled with water or acetic acid for use as a vapour trap for vapours seeping through the ground joint under pressure build-up. On completion of the reaction, the flask was immersed in an ice-cold bath for several seconds, the stopper was carefully raised but not fully removed for drainage of the well water into the flask and the contents were quenched with water (50 ml) and chloroform (10 ml). The contents were cooled to room temperature and titrated with 0.05 mol l<sup>-1</sup> sodium thiosulfate.

#### Application of perchloric acid and Fe<sup>3+</sup>

The above experimental conditions of the non-catalysed method were applicable to the catalysed reactions with the following modifications.

**Perchloric acid catalyst.** In reactions with HClO<sub>4</sub>, the acid catalyst was pipetted into the mixture after sparging with N<sub>2</sub> (15 s), the flow of N<sub>2</sub> continued for 3–6 s and the reaction continued as for the general method.

**Fe<sup>3+</sup> catalyst.** The sample was weighed; this was followed by addition of Fe<sup>3+</sup>-acetic acid solution (15 ml) containing the requisite Fe<sup>3+</sup> concentration, concentrated aqueous sodium iodide solution (2 ml) and then sparging with N<sub>2</sub> (15 s). The perchloric acid catalyst was pipetted into the mixture, the flow of N<sub>2</sub> continued for 3–6 s and the reaction continued in accordance with the general method. Starch was used as the end-point indicator because of the yellow tinge of the Fe<sup>3+</sup>.

### Results and Discussion

The iodimetric data for dialkyl peroxides and dicumenyl peroxide are shown in Tables 1–5 and a summary of the parameters and errors in the determinations is presented in Table 6. Dialkyl peroxides reacted thermally with iodide ion but a disadvantage of elevated temperature reactions for use in iodimetry was the increasing size of the blank caused by air oxidation of the iodide ion.<sup>1,5</sup> Some minor improvement in blanks was gained by expelling air from the solvent by boiling,<sup>5</sup> but this time-consuming step was an inconvenience to be avoided whenever possible. Consequently, experimental

**Table 3** Effect of HClO<sub>4</sub> on iodine liberated by *tert*-butyl octyl peroxide\* at 80 °C

Amount of 70% HClO <sub>4</sub> added/ml	Time/min	Amount of peroxide reacted† (%)
0	20	65‡
0.4	15, 20, 25	86, 84, 84
0.5	15	84.3
0.5	20	81.7, 87.2, 88.9 $\bar{x}$ = 86.7 ( $s$ = 3.88)
0.5	25	89.7, 92.8, 93.5 $\bar{x}$ = 92.0 ( $s$ = 2.02)
	30	101
0.6	10	85.0
	20	89.4, 91.2, 91.5, 92.8 $\bar{x}$ = 91.2% ( $s$ = 2.02)
0.8	10, 15, 20	82.1, 87.8, 91.5

\* 90.6% by GLC.

† Blanks were 3% correction to titre.

‡ 100 °C.

conditions that achieved short reaction times were preferred as prolonging reactions times beyond 20 min increased the blank with an associated diminishing of accuracy and precision.

### Dicumenyl Peroxide

On heating the dicumenyl peroxide–acetic acid–I<sup>−</sup> solution at 100 °C, less than half of the theoretical amount of iodine was liberated in 10 min, compared with quantitative formation within 5–15 min in the presence of 0.2–1.0 ml HClO<sub>4</sub> (Table 1, set A). Dilution of one iodimetric reaction with water (28% content) increased the reaction time (15 min) and gave incomplete iodine liberation (73%). The best set of values for completion in 5 min was obtained with 0.5 ml of HClO<sub>4</sub>. As commercial acetic acid contains trace amounts of iron ( $\approx 10^{-5}\%$ ), the optimum 0.5 ml HClO<sub>4</sub> concentration was studied in both distilled and undistilled acetic acid to

**Table 4** Effect of Fe<sup>3+</sup> on iodine liberated by *tert*-butyl octyl peroxide

Amount of FeCl <sub>3</sub> ·6H <sub>2</sub> O in acetic acid (% m/v)	Time/min	Temperature/°C	Peroxide (%)		
			Found	$\bar{x}$ ( $s$ )	GLC*
A† 2.7 × 10 <sup>−4</sup> ‡	15–20	100	87.4, 91.1, 93.6, 94.5 95.6, 96.0, 96.9, 87.0 93.8, 99.0	93.5 (3.93)	95.7
B§ 0.067–0.133	1–2	100	73.8, 73.6, 72.6	73.3 (0.64)	74.4
C§ 0.05–0.15	15–30	25	74.4, 75.1, 74.0, 71.2	73.7 (1.71)	74.4

\* Different peroxide concentrations are from separate distilled peroxide fractions.

† Blanks were 8% correction to titre.

‡ FeCl<sub>3</sub>·6H<sub>2</sub>O (% m/v) = 10<sup>−5</sup> mol l<sup>−1</sup> in acetic acid.

§ Blanks were 20% correction to titre.

**Table 5** Effect of parameters on iodimetric values of dialkyl peroxides

Alkyl	Amount of FeCl <sub>3</sub> ·6H <sub>2</sub> O in acetic acid (% m/v)	Time/min	Temperature/°C	Peroxide (%)		
				Found	GLC	HPLC
A* Hexyl	—	5	100	63	93.9	—
	—	10	100	88.3	—	—
	—	15	100	94.4	—	—
	—	20	100	92.9, 91.8	—	—
	—	25	100	95.7, 92.6	—	—
	—	30	100	95.3	—	—
	—	15–30	—	$\bar{x}$ = 93.8 ( $s$ = 1.58)	—	—
B† Hexyl	2 × 10 <sup>−3</sup>	30, 60	25	81, 80	95.7	—
	4 × 10 <sup>−2</sup>	1, 50	25	78, 77	—	—
	2 × 10 <sup>−3</sup>	1, 2, 5	100	84, 84, 80	—	—
C Octyl Decyl Dodecyl Tetradecyl Hexadecyl	—	20	100	89.1	90.1	—
	—	20, 25	100	93.4, 95.7	—	95.4
	—	20	100	32	—	95.6
	—	25	100	40	—	98.8
	—	20	100	26	—	99.1

\* Blanks were 2–4% correction to titre.

† Blanks were 2–12% correction to titre.

**Table 6** Summary of parameters (catalysts, time and temperature) and error on iodimetric determination of dialkyl peroxides

Peroxide	Amount of 70% HClO <sub>4</sub> /ml	Amount of FeCl <sub>3</sub> ·6H <sub>2</sub> O in acetic acid* (% m/v)	Time/min	Temperature/°C	Error† (%)
Di- <i>tert</i> -butyl‡	0.5	—	20	100	1
Dicumenyl	0.5	—	5	100	2
<i>tert</i> -Butyl alkyl	0.6	—	20	80	2
<i>tert</i> -Butyl alkyl	—	2.7 × 10 <sup>−4</sup>	20	100	4
<i>tert</i> -Butyl alkyl	—	0.1	2	25	1§
Dialkyl	—	—	20	100	2

\* 15 ml.

† Error (%) = 100/ $\bar{x}$  and rounded to nearest whole number.

‡ Acetic acid boiled to expel dissolved air prior to analysis.

§ Uncorrected for error contributed by 20% of blank to titre.

determine the effect of trace amounts of iron. The average value with the former solvent was 99.4% ( $s = 1.98\%$ ) and with the latter 100.8% ( $s = 3.50\%$ ) compared to  $99.6 \pm 0.3\%$  by HPLC. The two sets were not significantly different, calculated according to the Student's  $t$ -test,  $t = 1.07$ , suggesting that adventitious impurities such as iron ( $2 \times 10^{-6}\%$ ) in undistilled acid are innocuous at this low concentration. A test of  $\text{Fe}^{3+}$  at the higher concentrations of  $2 \times 10^{-3}$ – $2 \times 10^{-1}\%$  (Table 1; set B) showed no catalytic advantage in time and accuracy compared with perchloric acid *per se*. Perchloric acid has a marked effect as a rate accelerator: the reaction was completed in 5 min at the lower temperature of  $100^\circ\text{C}$  as compared with  $120^\circ\text{C}$  and 20 min reaction with 37% HCl reported using Method 2.<sup>5</sup> The advantage of perchloric acid might be attributed to strong acid catalysis in addition to the *in situ* formation of HI.

### Di-*tert*-Butyl Peroxide

Di-*tert*-butyl peroxide is more stable than dicumenyl peroxide and more difficult to reduce iodimetrically. Nevertheless, iodimetric reduction in the presence of perchloric acid (Table 2) occurred with relative ease. With  $\text{HClO}_4$  (2 ml), completion was in 20 min but the average value 97.2% ( $s = 1.15\%$ ) was about 3% lower than indicated by GLC for the pure compound (99.9%). The smaller value of the apparent peroxide content can be attributed to the volatility of the compound [b.p.  $109^\circ\text{C}$  (atm)]<sup>11</sup> resulting in some loss by seepage through the ground joint of the iodine flask.

### *tert*-Butyl Octyl Peroxide

In the absence of catalyst, 65% of the iodine was liberated by *tert*-butyl octyl peroxide in 20 min at  $100^\circ\text{C}$ . Perchloric acid (Table 3) and  $\text{Fe}^{3+}$  (Table 4) were both effective in aiding rate enhancement and quantification. In the presence of 0.5 and 0.6 ml of  $\text{HClO}_4$  the reaction was completed at  $80^\circ\text{C}$  in 25 and 20 min, respectively, with good agreement (92.0%,  $s = 2.02$ ; and 91.2%,  $s = 2.02\%$ ) with GLC (90.6%) for the small numbers examined. At the low % m/v concentration of  $\text{Fe}^{3+}$  ( $2.7 \times 10^{-4}\%$ ), completion was in 15 min at  $100^\circ\text{C}$  with an average value of 93.5% ( $s = 3.93\%$ ) versus 95.7% via GLC. At high catalyst concentrations ( $\approx 0.1\%$ ) (Table 4) reaction times were reduced to 1–2 min at  $100^\circ\text{C}$  for set B and proceeded to quantification within 15–30 min at room temperature for set C. The evident time advantage for the former, and low temperature advantage for the latter, at their higher  $\text{Fe}^{3+}$  concentrations were offset by an increase in uncertainty that derived from large blank corrections of 20% (0.3 mequiv of  $\text{I}_2$ ) to the sample titres.

A briefly examined approach utilizing propan-2-ol–acetic acid– $\text{I}^-$  modified with perchloric acid (0.5 ml) and 0.1%  $\text{Fe}^{3+}$  in acetic acid (2 ml) offered a potential alternative method. The reaction was complete in 10 min at  $80^\circ\text{C}$  on two samples giving 70.7 and 69.5%, in agreement with GLC (69.1%).

### Dialkyl Peroxides

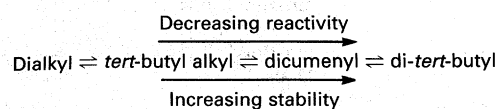
The dihexyl peroxide– $\text{I}^-$  reaction did not require catalysis (Table 5, set A). It was thermally reactive at  $100^\circ\text{C}$  reaching quantification within 15–30 min. Because the values in this time span provided a statistical set, they were averaged to 93.8% ( $s = 1.58\%$ ) in excellent agreement with GLC (93.9%). The inclusion of  $\text{Fe}^{3+}$  as catalyst (set B) reduced the reaction time to 1 min at  $100^\circ\text{C}$  and to 1 min at  $25^\circ\text{C}$  at higher concentrations. However, the presence of iron induced a levelling of the iodimetric value to  $\approx 85\%$  of the expected peroxide content. The depressed value can be attributed to a parallel metal-induced decomposition of peroxide to alcohol and aldehyde, which were products that were observed in neat dialkyl peroxides stored for extended periods of time ( $>6$  months) in tin-capped vials at  $5^\circ\text{C}$ , and were reported by

others<sup>11</sup> as contaminants in GLC analysis on preparative chromatographically purified dialkyl peroxides.

The conditions shown in Table 5 for set A at  $100^\circ\text{C}$  for dihexyl peroxide without catalyst were applied to the series of even chain peroxides (set C) from octyl to hexadecyl, inclusive. Values for dioctyl and didecyl peroxides were in agreement with their GLC and HPLC analysis, respectively, but the longer chain members gave apparent values of only 25–40%. *n*-Dialkyl peroxides are the least stable members in the dialkyl peroxide class. The failure of long chain members was caused by their insolubility in acetic acid wherein they decomposed on thermal dissolution within the insoluble liquid globules or solid phases. The addition of chloroform to the acetic acid to enhance solubilization was not examined for these homologues owing to the low values observed for chloroform as co-solvent in several preliminary studies with *tert*-butyl octyl peroxide. This was not unexpected for halogenated solvents that are known to participate in wasteful radical–solvent reactions by chain transfer processes.<sup>12</sup>

### Conclusion

The simplified iodimetric method for dicumenyl peroxide gave an excellent average value in agreement, to within  $s = 2\%$ , of the GLC value. Although the proposed method is more convenient and rapid than the methods of Mair and Graupner,<sup>5</sup> comparison of data for accuracy and precision is difficult. The accuracy of the average values reported for dicumenyl peroxide<sup>5</sup> by an HI method on four samples (97.2, 97.9, 92.6 and 96.5%;  $\bar{x} = 97.3\%$ ,  $s = 0.61\%$ ) and by Method 3 on two samples (96.3 and 96.4%) lacks confirmation by an independent method. The precision above is excellent for the small number of samples analysed, although the numbers of samples are too limited to provide a statistical distribution of values for comparison. The four peroxide types assembled in Table 6 show distinct differences in reactivity with  $\text{I}^-$ . Di-*tert*-butyl and dicumenyl peroxide each reacted readily in the presence of perchloric acid and the latter peroxide with  $\text{Fe}^{3+}$ –perchloric acid but the more stable di-*tert*-butyl peroxide, which is unreactive with  $\text{Fe}^{3+}$ , required a longer reaction time with perchloric acid. The *tert*-butyl alkyl peroxide with only half the peroxide molecule sterically hindered was readily catalysed by either perchloric acid or by  $\text{Fe}^{3+}$  to provide the percentage peroxide content with good accuracy and precision, although perchloric acid gave the higher precision. Dialkyl peroxides by comparison were found to be more reactive by thermally proceeding to quantification without catalysis. Nevertheless, the dialkyl peroxides were able to liberate iodine at room temperature using the  $\text{Fe}^{3+}$  catalyst but with stoichiometric incompleteness, which is attributed to a parallel metal-induced peroxide decomposition. Whereas the small and medium chain homologues, up to didecyl peroxide, react quantitatively, the insolubility of the longer chain dialkyl peroxides demonstrates the limitation of iodimetry for these members and the requirement of an alternative analytical method such as chromatography. The four classes of peroxides examined in this work revealed differences in their propensities for iodine liberation. They can be assembled in the following order of decreasing reactivity and increasing stability. The reactivity order suggests that iodimetry might be useful in qualitative analysis such as spot tests for dialkyl peroxide identification or peroxide differentiation by judicious use of perchloric acid,  $\text{Fe}^{3+}$  and heat.



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